



Diagnostic Studies to Improve Abuse Tolerance and life of Li-ion batteries

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Overview

Timeline

- **Start: 10/01/2010**
- **Finish: 9/30/2013**

Budget

- **Funding received in FY12**
DOE: \$350k
- **Funding received in FY13**
DOE: \$350k

Barriers addressed

- To reduce the production cost of a PHEV battery
- Li-ion and Li-metal batteries with long calendar and cycle life
- Li-ion and Li-metal batteries with superior abuse tolerance

Collaborators

- Argonne National Lab. (ANL)
- Pacific Northwest National Lab. (PNNL)
- Beijing Institute of Physics
- Korea Institute of Science and Technology
- Duracell (P&G)
- Dow Chemical
- GM R&D Center
- Johnson Controls-Advanced Power solutions

Project Objectives

✓ *Diagnostics study of thermal abuse tolerance (safety related issues).*

- to establish and investigate the structural origin of thermal instability of various cathode materials.
- to search new approaches on how to improve the thermal stability of cathode materials including surface modification techniques and the effectiveness of them.
- to provide valuable information about how to design thermally stable cathode materials for HEV and PHEV applications.
- to develop new *in situ* diagnostic techniques with surface and bulk sensitivity for studying the thermal stability of various cathode materials.

✓ *Diagnostics study of the cell capacity, voltage and power fading.*

- to develop *in situ* diagnostic techniques with surface and bulk sensitivity for studying the capacity, voltage, and powder fading mechanisms of Li-ion battery.
- to establish and investigate the capacity and power fading mechanisms of various cathode materials.

✓ *Diagnostics study of electrode materials with lower cost potential.*

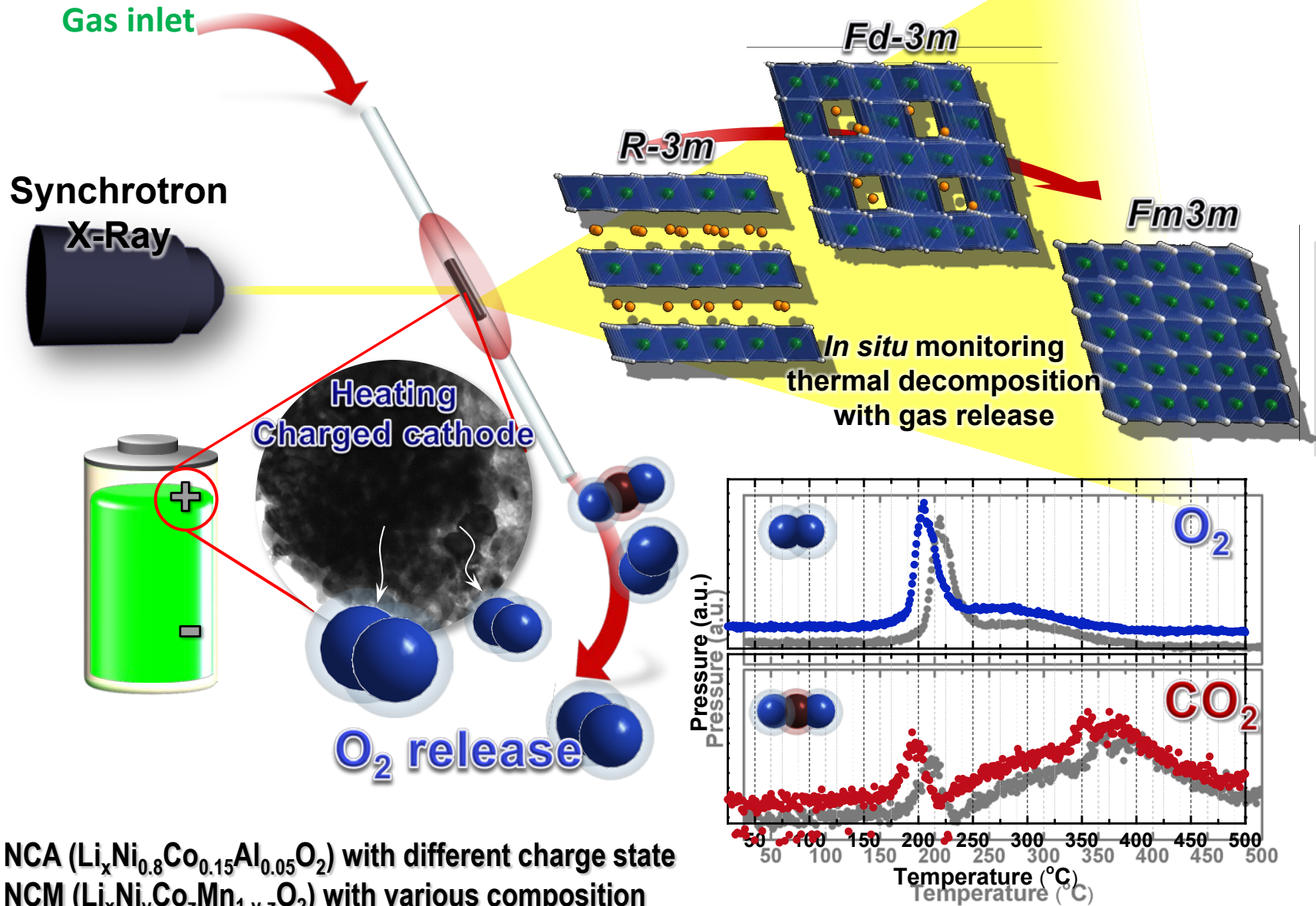
Milestones

Month/Year	Milestones
Sep/12	complete the study of charged $\text{Li}_x\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) cathode material thermal decomposition during heating using combined Time-Resolved XRD and Mass Spectroscopy. ➡ Completed.
Apr/13	Complete the study of thermal decomposition of charged of charged $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ (Toda HE5050) cathode materials during heating using combined Time-Resolved XRD and Mass Spectroscopy ➡ Completed.
Apr/13	Complete the ex situ soft x-ray XAS studies of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ (Toda HE5050) cathode material during charge-discharge cycling to distinguish the structural change differences between the surface and the bulk ➡ On schedule.
Sep/13	Complete the in situ hard x-ray XAS studies of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ (Toda HE5050) cathode material for the voltage fading mechanism and structural instability during extended cycling ➡ On schedule.
Sep/13	Complete the studies of thermal decomposition of charged $\text{Li}_{1.2}\text{Ni}_{0.17}\text{Mn}_{0.53}\text{Co}_{0.1}\text{O}_2$ (ANL-HE5050) cathode materials with and without AlF_3 coating during heating using combined Time-Resolved XRD and Mass Spectroscopy ➡ On schedule.

Approaches

- A combination of **time resolved X-ray diffraction (TR-XRD)** and **mass spectroscopy (MS)**, together with *in situ* **soft and hard X-ray absorption (XAS)**, *in situ* **transmission electron microscopy (TEM)** techniques during heating to study the **thermal stability** of the electrode materials.
- Apply the atomic layer deposition (ALD) technique for the surface modification of new cathode materials, using **time resolved X-ray diffraction (XRD)** to study the effects of surface modification on the **thermal stability**.
- Using *in situ* **XRD, soft and hard XAS** to study the voltage and capacity fading mechanism of high energy density Li and Mn rich layer structured NCM (LMR-NCM) electrode materials during charge-discharge cycling for **longer cycling life** of Li-ion batteries.
- Extended collaboration with other US and international academic institutions and US industrial partners.

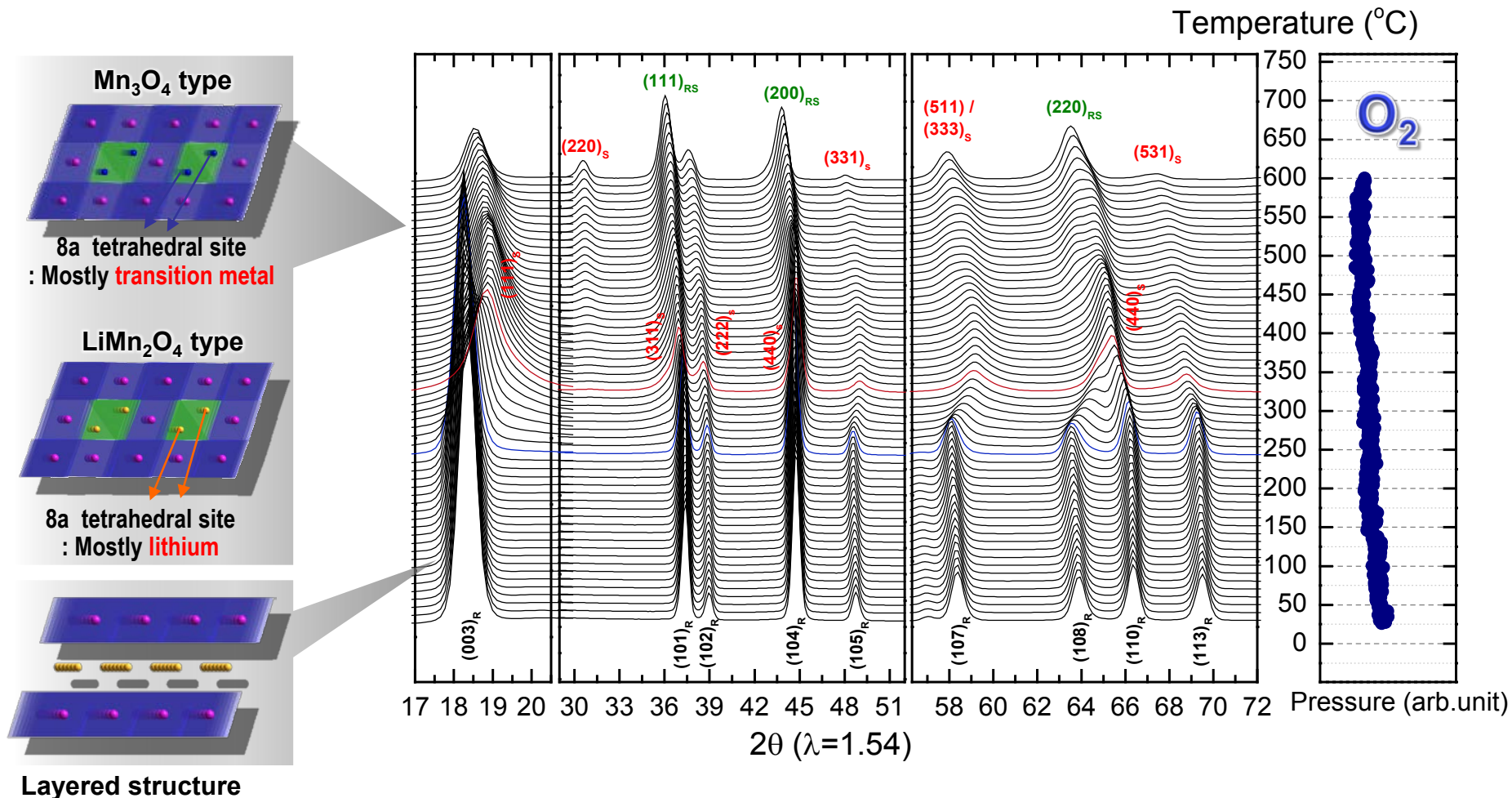
Approach: using combined time-resolved XRD and mass spectroscopy



Technical Accomplishments

- By collaborating with Dr. Bonhomme and Dr. Cho at Johnson Controls, applied the newly developed *in situ* technique using a combination of time resolved XRD (TR-XRD) with mass spectroscopy to study the thermal stability of charged $\text{Li}_x\text{Ni}_{1-2y}\text{Co}_y\text{Mn}_y\text{O}_2$ ($y=0.33, 0.3, 0.2$, and 0.1) cathode materials during heating. The co-relation between structural changes and oxygen release of these materials were obtained, showing the higher thermal stability of materials with lower Ni content.
- Through collaborative research with Dr. Abraham and Dr. Amine at ANL, carried out thermal stability studies of high energy density $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ ($\text{M}=\text{Ni, Co, Mn}$, LMR-NCM) cathode materials with and without Co content, as well as with and without AlF_3 coating. It was found that the thermal stability of AlF_3 coated sample is better than the non-coated sample.
- By collaborating with ANL, R&D Center of GM, and other collaborators, carried out diagnostic studies of new high energy density $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ ($\text{M}=\text{Ni, Co, Mn}$, LMR-NCM) cathode materials. Some important structural origins of the voltage and capacity fading mechanism has been obtained.

Thermal behavior of charged cathode material ($\text{Li}_x\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}\text{O}_2$) (Through collaboration with Johnson Controls)

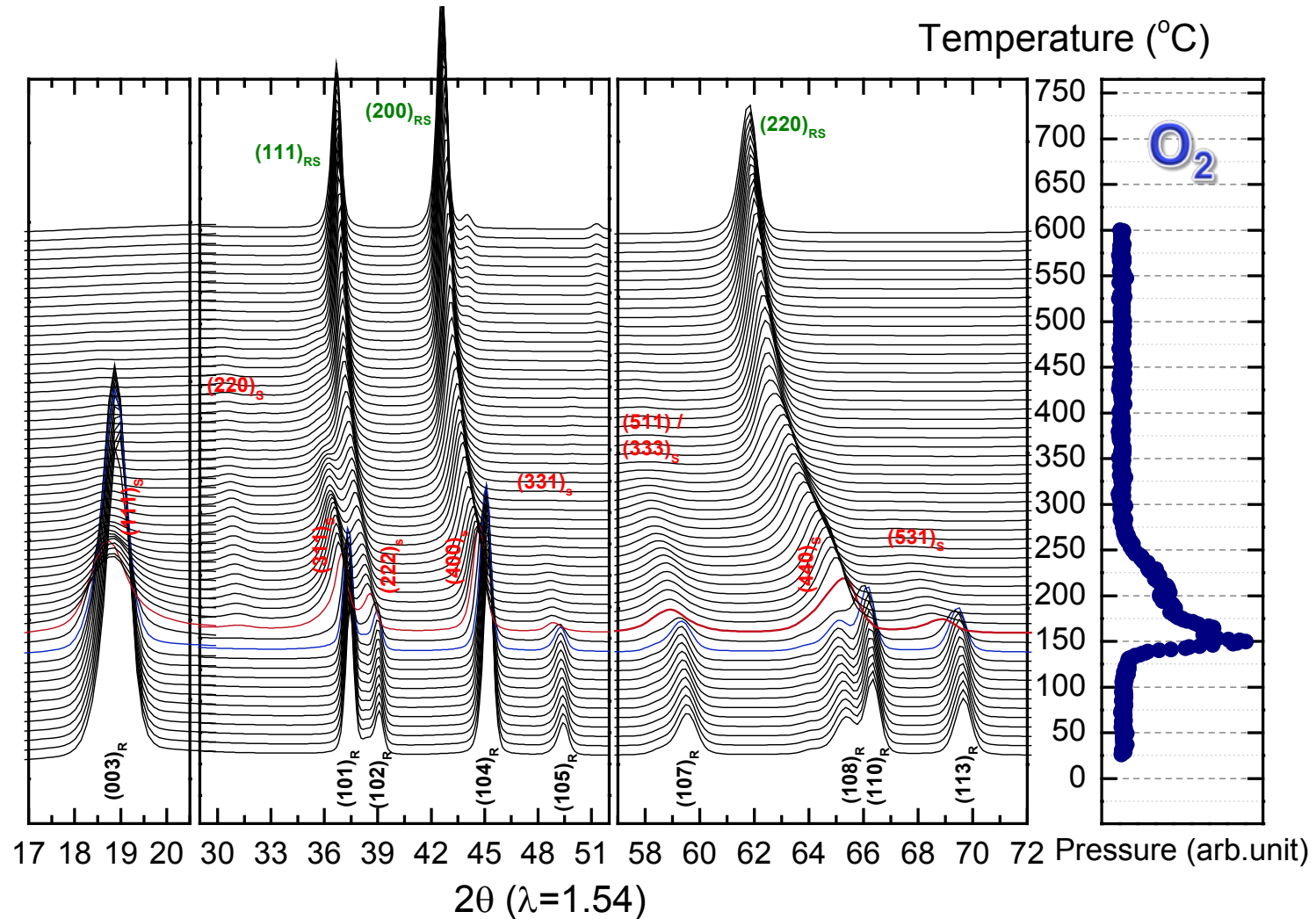


- **Much better thermal stability than NCA cathode material!!**

↳ 1st phase transition occurred at around 250 $^{\circ}\text{C}$, and no significant oxygen release.

- **Much wider temperature range for the disordered spinel region due to the stabilization of two different spinel type structures.**

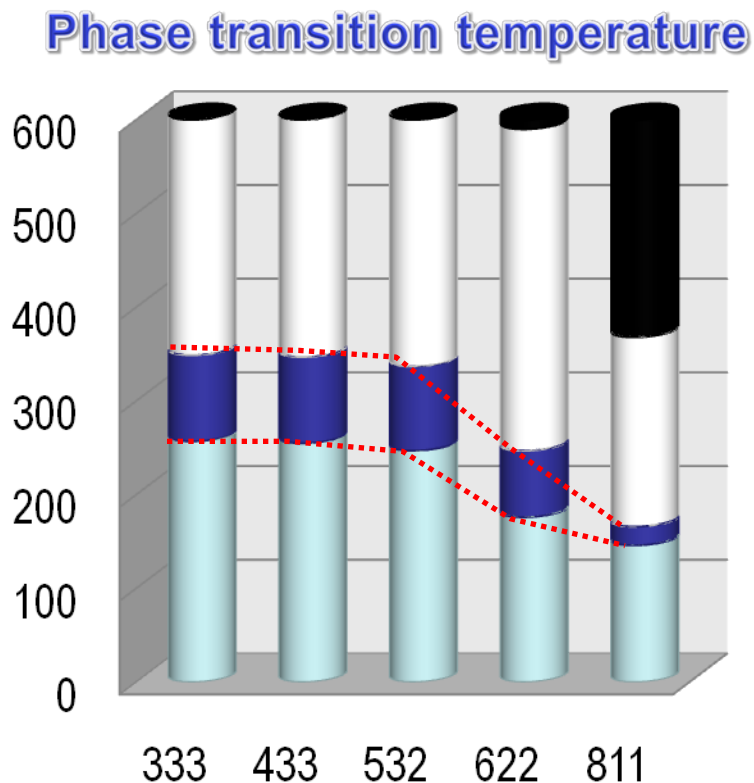
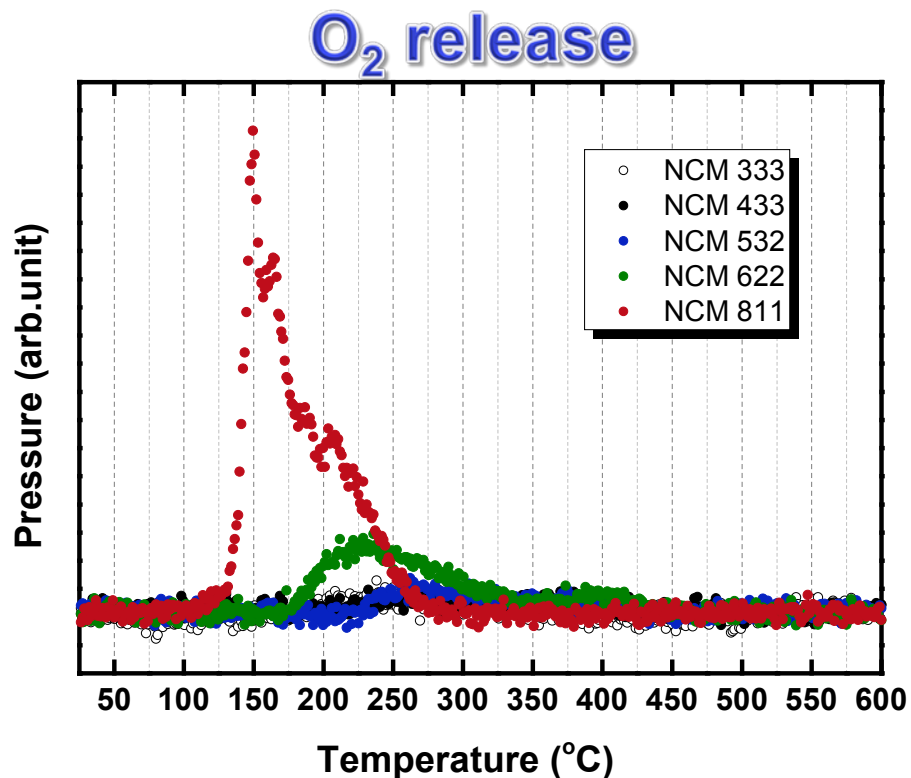
Thermal behavior of charged cathode material ($\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$) (Through collaboration with Johnson Controls)



- As increase in Ni content, the cathode material in charged states becomes more thermally instable.

↳ 1st phase transition occurred at around 150 $^{\circ}\text{C}$, and observed significant oxygen release.

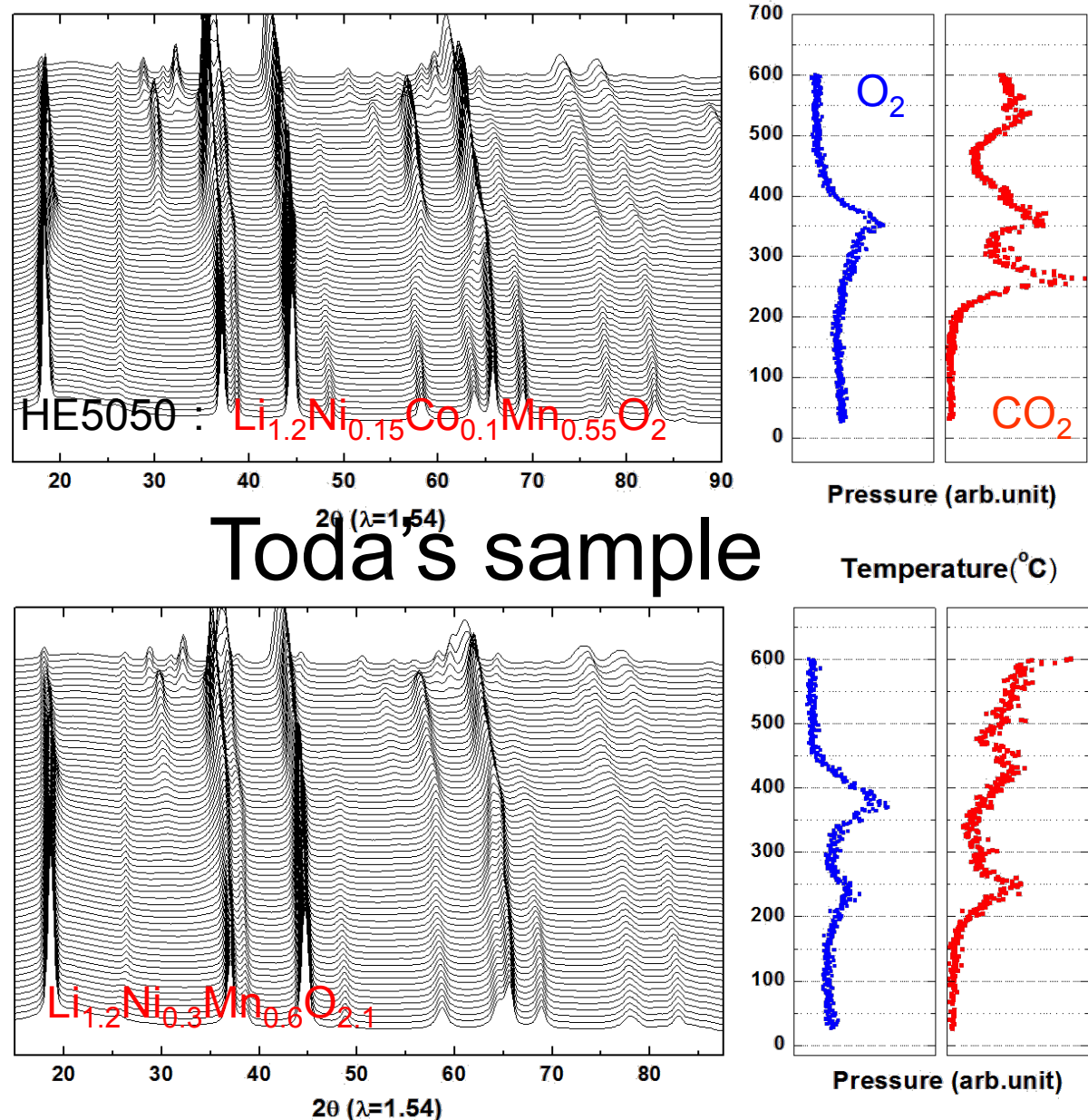
Thermal Stability of Charged $\text{Li}_x\text{Ni}_{1-2y}\text{Co}_y\text{Mn}_y\text{O}_2$ Cathode Materials (Through collaboration with Johnson Controls)



The capacity and thermal stability are strongly related to the percentage content of Ni, Co, and Mn. In general, the higher the content of Ni, the higher the capacity, but the poorer the thermal stability. This trade-off can be used to guide the development of the cathode materials with balanced properties.

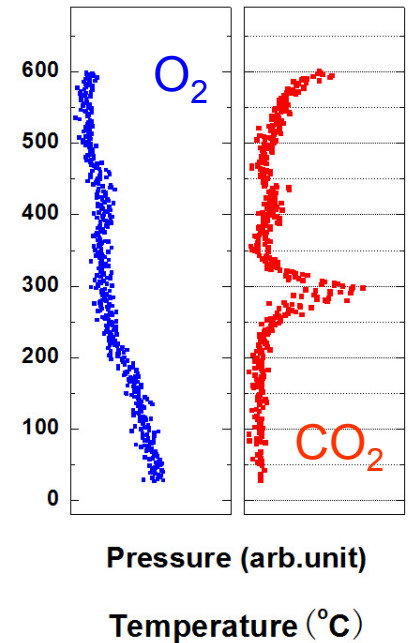
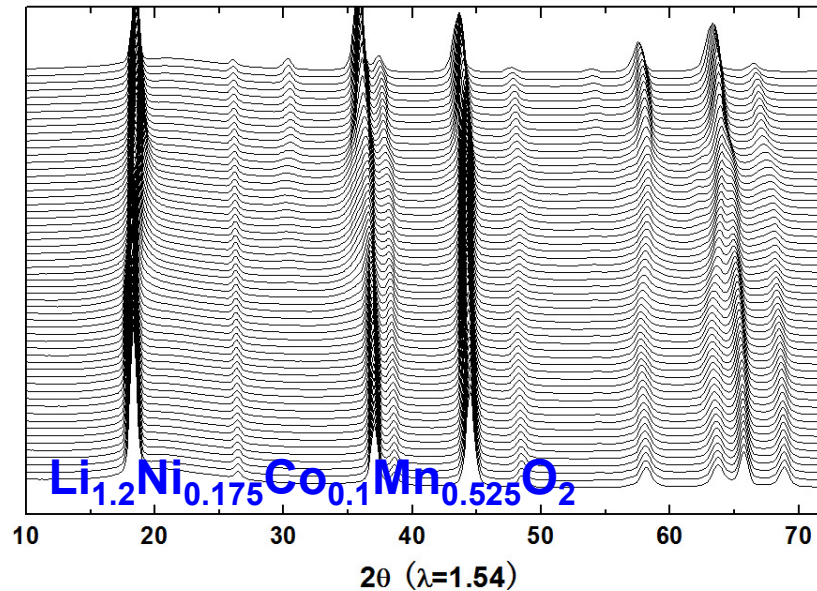
Thermal behavior of charged Li-rich cathode materials (Collaborator at ANL: Daniel Abraham)

- (1) *Similar as regular NCM layered materials, the investigated Li rich layered compounds (with and without Co, at charged states) reveal the same phase transition pathway: layered to spinel, then to rock-salt structure.*
- (2) *Oxygen and Carbon dioxide release can be observed during thermal process.*

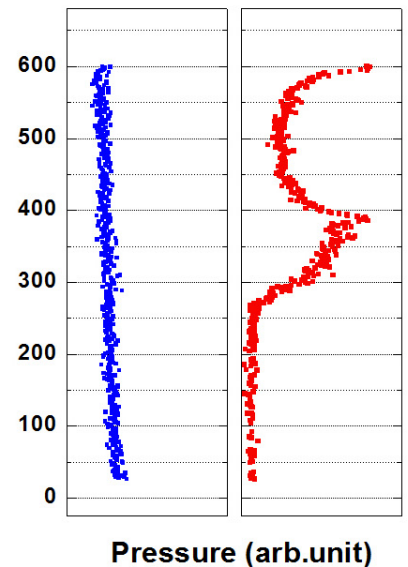
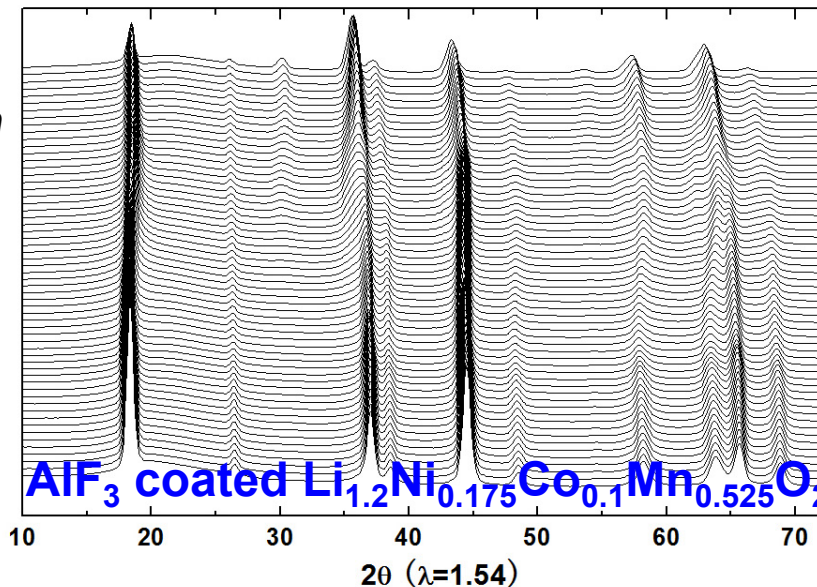


Thermal behavior of charged Li-rich cathode materials (Collaborator at ANL: Huiming Wu and Khal Amine)

(1) *No significant Oxygen release can be observed for both uncoated and coated $\text{Li}_{1.2}\text{Ni}_{0.175}\text{Co}_{0.1}\text{Mn}_{0.525}\text{O}_2$ samples, which indicates oxygen release proceed through a more “tender” way;*



(2) *Carbon dioxide release can be observed, which may be due to the reaction of the released oxygen with carbon. Carbon dioxide release is postponed for the AlF_3 coated sample comparing with uncoated.*



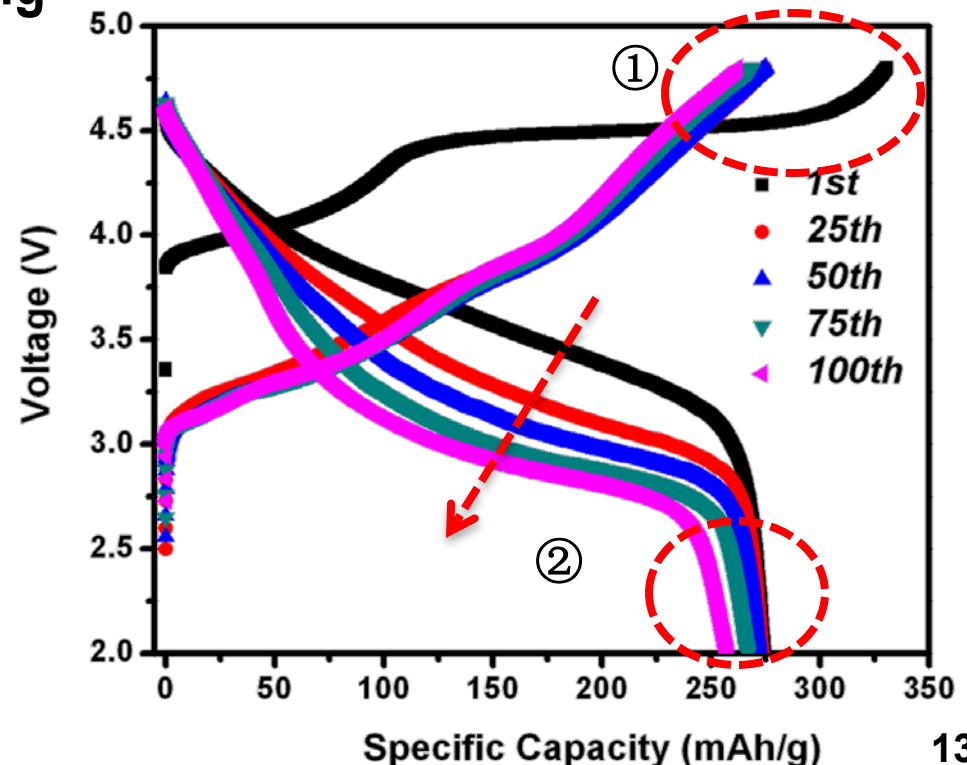
Li and Mn rich layered-layered oxide compound (LMR-NCM)



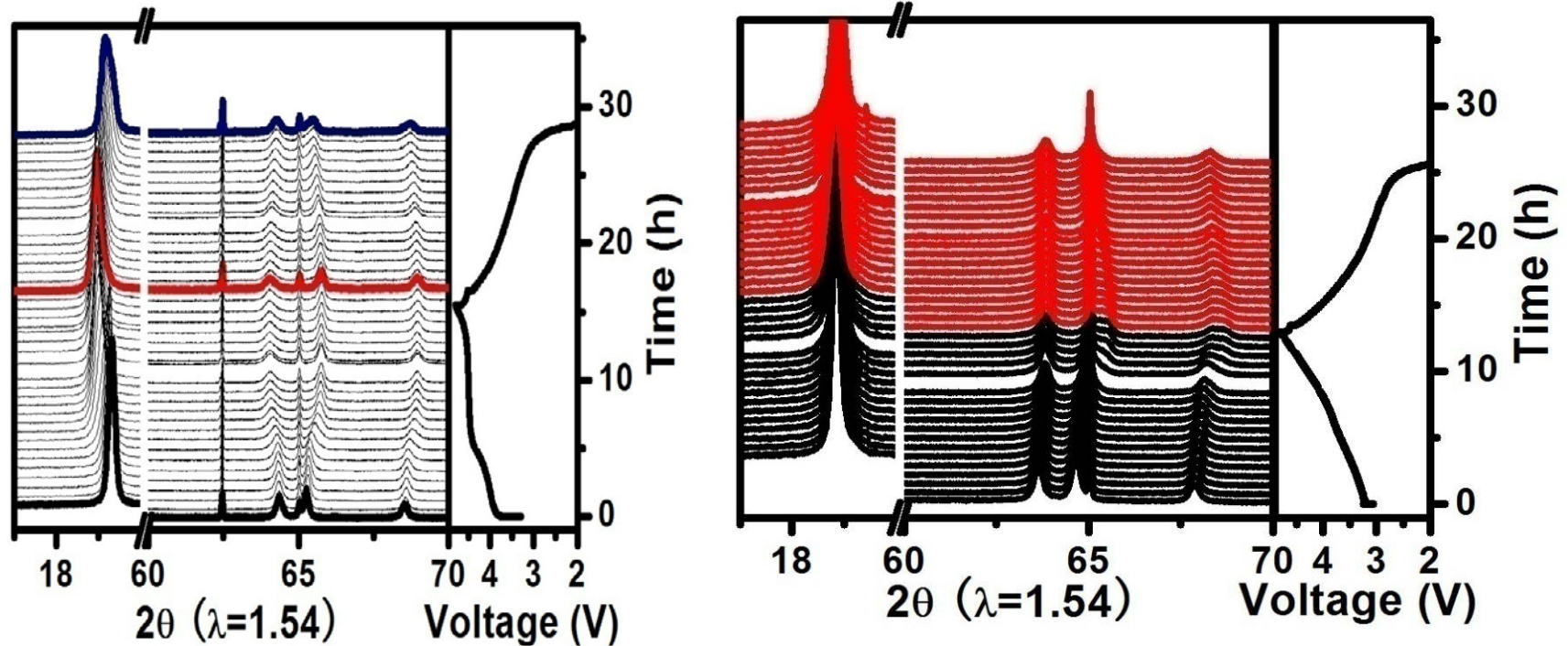
- High specific capacity (>250 mAh/g)
- Integration and interconnection of LiMO_2 -like (rhombohedral) and Li_2MnO_3 (monoclinic) structures at atomic level
- Activation of Li_2MnO_3 during the 1st charge process
- Structure changes during cycling

Issues to be addressed:

1. Large irreversible capacity loss during first charge
2. Voltage and capacity fading during cycle
3. Key factor that “control” the rate performance

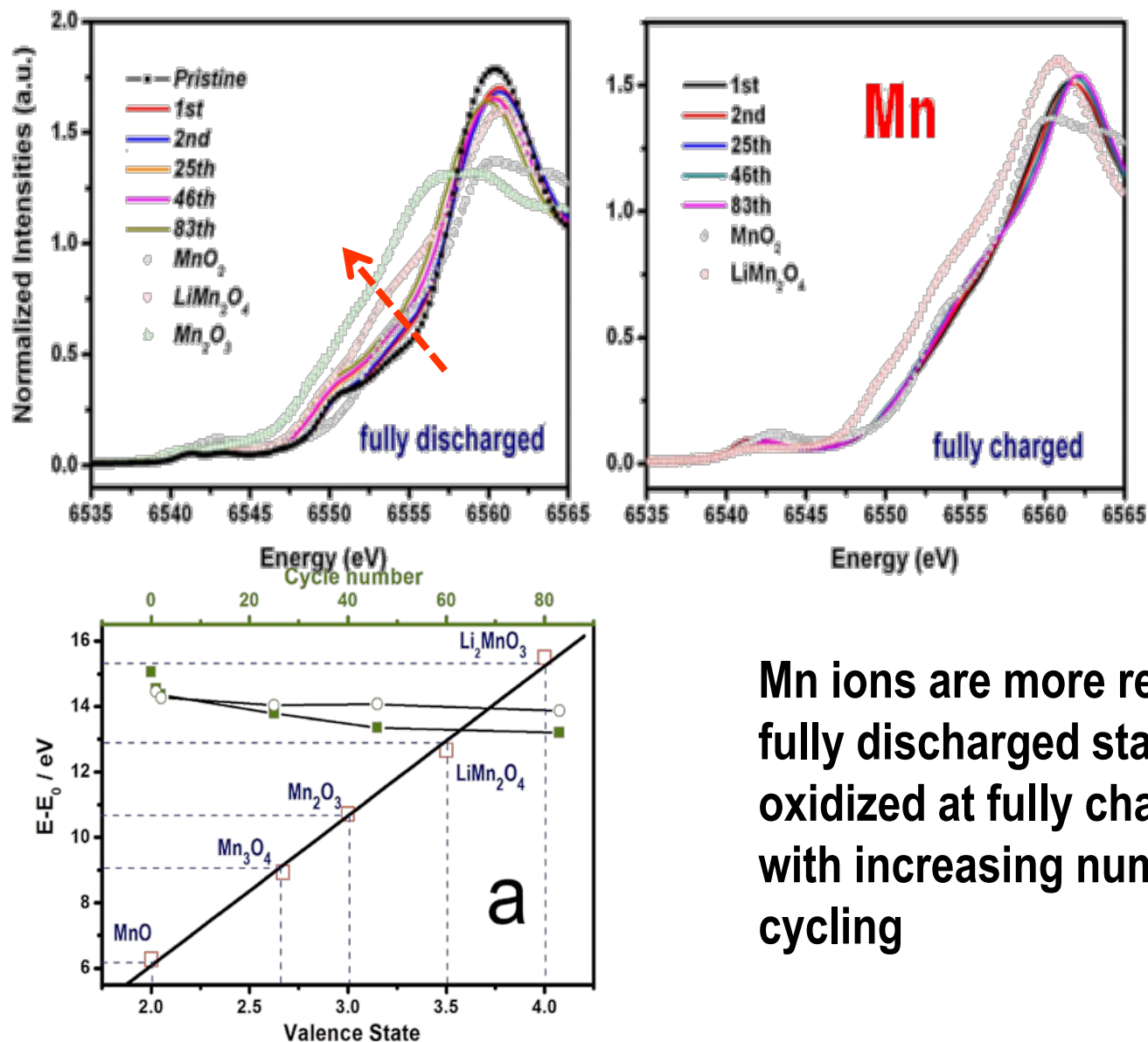


Different structural changes during first and 45th cycle for $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ sample studied by *in situ* XRD



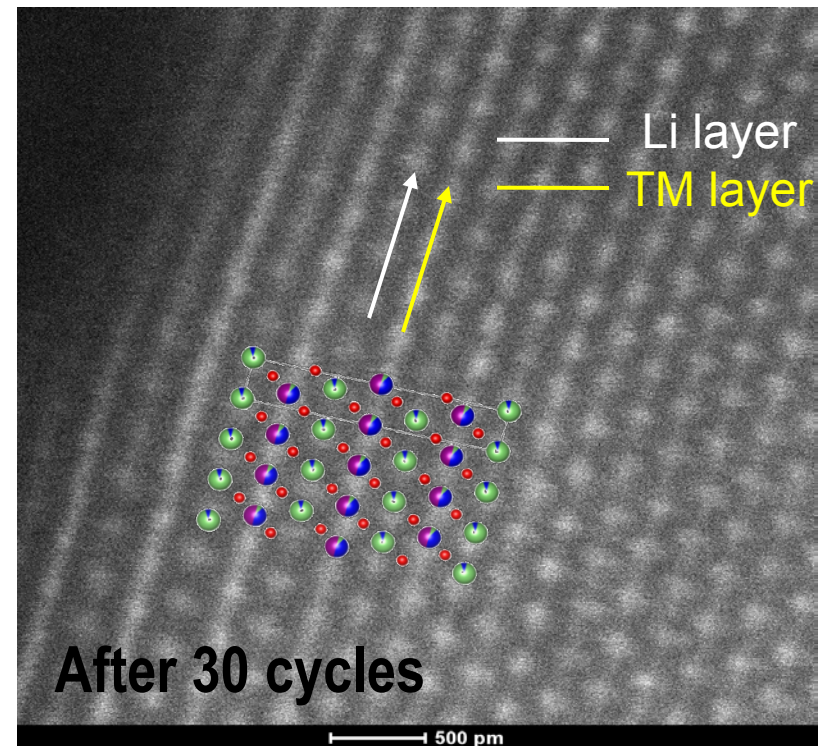
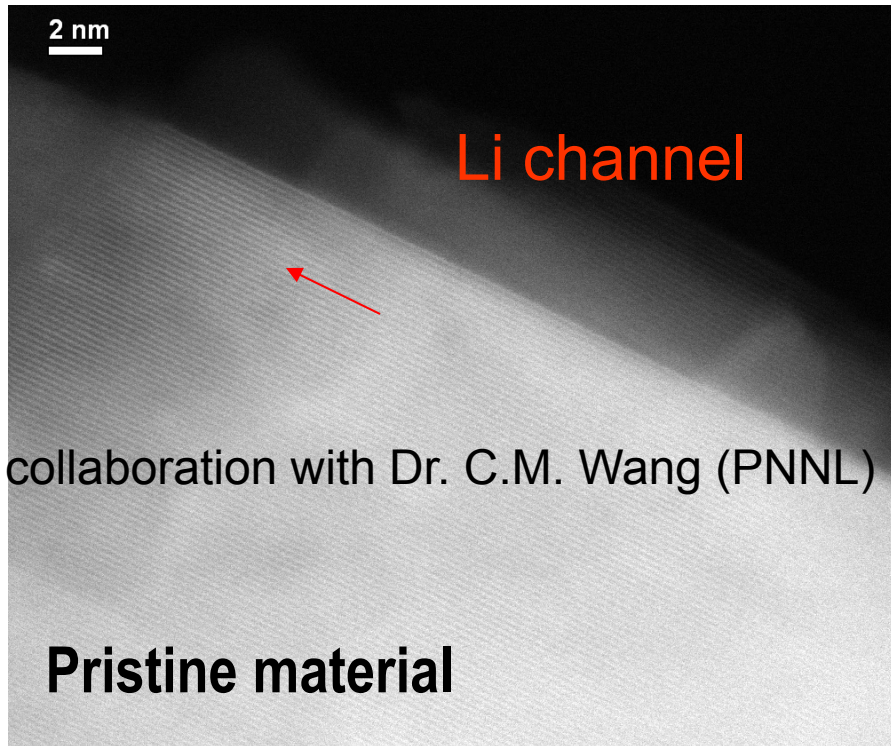
- Spinel-like phase transition behavior observed after 45 cycles;

Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O₂ - XAS studies



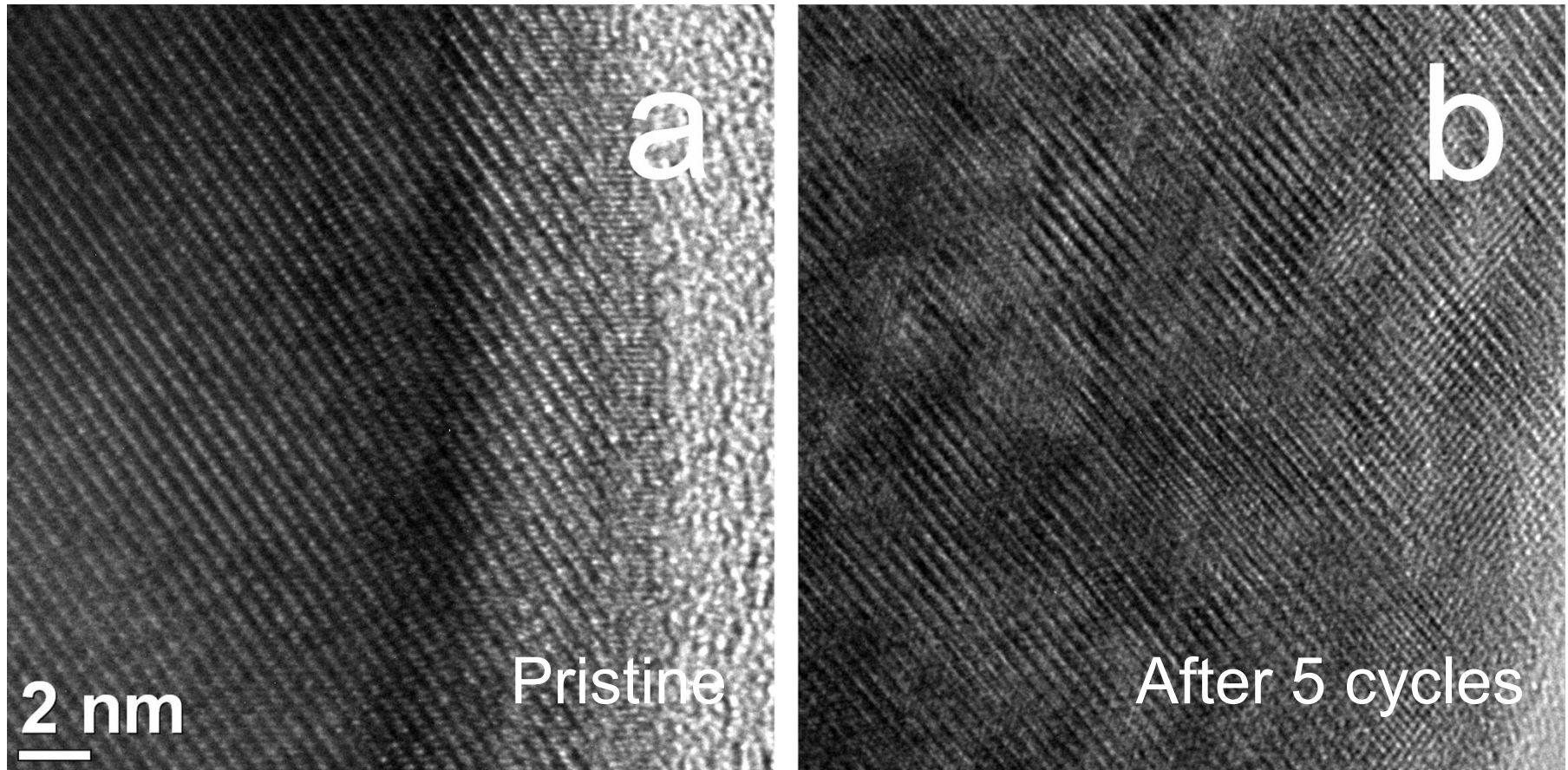
Mn ions are more reduced at fully discharged state and less oxidized at fully charged state with increasing number of cycling

HRTEM results: $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ - Structure changes after cycling



- **Pristine material:** Li channels are dark, no significant amount of TM ions should be in the Li layer;
- **Cycled material (after 30cycles):** White arrow indicates the Li layer, which is now taken by the TM ions. The contrast of the atomic columns in the Li layer and TM layers are similar, which indicate the formation of the spinel structure on surface.

TEM observation of structural damages in Li_2MnO_3 region in $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ sample caused by activation and cycling



- Structure “damage” after initial activation (mostly in Li_2MnO_3 region)

Collaborations with other institutions and companies

■ Argonne National Lab. (ANL)

↪ *In situ* XRD and XAS study of high energy density $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ composite (LMR-NCM).
(LMR-NCM sample preparation and distribution by the “post-testing facility” at ANL).

■ Pacific Northwest National Lab. (PNNL)

↪ HR-TEM study of high energy density $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ composite (LMR-NCM).
(LMR-NCM sample preparation and distribution by the “post-testing facility” at ANL).

■ Beijing Institute of Physics

↪ ALD surface coated cathode materials and new electrolyte additives.

■ Johnson Controls- Advanced Power Solutions

↪ Layer structured $\text{LiNi}_{1-2y}\text{Co}_y\text{Mn}_y\text{O}_2$ ($y = 0.33, 0.3, 0.2$ and 0.1) cathode materials.

■ GM R&D Center

↪ *In situ* XRD and XAS study for high energy density $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ composite.

Planned work for *FY 2013* and *FY2014*

- Taking the advantage of the element specific nature of X-ray absorption spectroscopy (XAS), develop a new synchrotron based time resolved XAS and apply it to study the structural evolution and delithiation kinetic difference among Ni, Co, and Mn ions of the Li-rich layered $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ cathode material during high rate delithiation.
- Using TEM and synchrotron based XAS, study the effects on surface structural changes and voltage fading by the surface coating and the use of additive in forming solid electrolyte interphase (SEI) on the Li-rich layered $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ cathode material surface
- In collaboration with Johnson Controls, using *In situ* XRD, hard and soft XAS, to study the structural changes of series of layer structured cathode materials such as $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$, and $\text{LiNi}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}\text{O}_2$ during cycling to identify the effects of Ni, Co, and Mn content on capacity and cycle life during charge-discharge cycling.
- Expand the collaborative research with US and international academic research institutions and US industrial partners.

Summary

- Through collaborative research with US industries and international research institutions, progress has been made by this ES034 project to achieve the goals of developing next generation of batteries for HEV, PHEV, and EV set by the Vehicle Technology Program of EE&RE of USDOE.
- In collaboration with Johnson Controls, *in situ* diagnostic tools using the combination of time resolved x-ray diffraction (TR-XRD) and mass spectroscopy (MS) during heating have been developed and applied to study the charged cathode materials such as $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, $\text{Li}_x\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ and $\text{Li}_x\text{Ni}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}\text{O}_2$. It was found that the higher the content of Ni, the higher the capacity, but the poorer the thermal stability in these NCM materials.
- In collaboration with ANL, *in situ* XRD and XAS, as well as the combination of TR-XRD and MS techniques were used to study the voltage and capacity fading mechanism, and thermal stability of high energy density $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ (LMR-NCM) composite cathode materials with and without surface coating. The results of these studies show that this material forms more and more spinel like structure during cycling, suggesting the intrinsic structural instability of this material. The effectiveness of AlF_3 surface coating on the improvement of thermal stability was also shown.
- In collaboration with PNNL, HRTEM and other TEM techniques were used to study the structural changes of $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Co}_{0.1}\text{Mn}_{0.55}\text{O}_2$ cathode material during activation and cycling. The results show that the spinel like structure was formed near the surface of the sample after 30 cycles.